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Two-Determinant Spin-Polarized Calculation of the Hyperfine Structure of B^{11}

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A two-determinant spin-polarized function derivable from the spin configurations $\Pi_i(\alpha\beta)_i\Pi_j\alpha_j$ and $\Pi_i(\beta\alpha)_i\Pi_j\alpha_j$ is presented and applied to the boron atom using modified Slater orbitals which are solved non-self-consistently. For purposes of comparison, single-determinant polarized and nonpolarized functions with the same orbital base are also determined. For all three functions the hyperfine constant is calculated, and it is found that the constant a_s [equal to 0.11 atomic units (a.u.) experimentally] changes from -49.96 to -40.33 a.u. from the one- to the two-determinant spin-polarized functions with the corresponding energy improvement from -24.503 to -24.527 a.u. (as compared to the experimental energy of -24.66 a.u. and the best spin-polarized Hartree-Fock value of -24.529 a.u.). In addition it is pointed out that cancellation difficulties in determining charge density at the nucleus from *ns* pairs is greatly alleviated, and that in order to use a proper eigenfunction of $\mathbf{S}^2$ we are required to include many more determinants than we are presently prepared to deal with.

INTRODUCTION

SPIN angular momentum with its associated magnetic moment was first introduced by Pauli[1] to account for hyperfine structure in atomic spectra. Using the Dirac relativistic theory of the electron, Fermi[2] derived the interaction Hamiltonian between the magnetic moments (spin and orbital) of a single electron and a nucleus. This Hamiltonian has been subsequently derived by Aronowitt[3] using quantum field theory. For many electrons one merely sums the interaction Hamiltonian for a single electron over all the electrons. This summation is most easily accomplished using the methods of Racah,[4] as has been shown by Trees[5] for the case of *LS* coupling which concerns us here. The results are expressed in the notation introduced by Goudsmit.[6] Thus, the energy W_F of a particular hyperfine structure level may be expressed in terms of the energy W_J of the corresponding fine-structure level by the relation[7]

$$W_F=W_J+\tfrac{1}{2}a_JK+BK(K+1), \tag{1}$$

where

$$K=F(F+1)-L(L+1)-J(J+1). \tag{2}$$

In Eq. (1) the term $\frac{1}{2}a_JK$ arises from the magnetic dipole interaction between the electrons and the nucleus, while the term $BK(K+1)$ is the electric quadrupole interaction. We are concerned here with the hyperfine constant a_J, which is independent of F.

For the particular case of boron in a $(1s)^2(2s)^22p$ configuration, $J=\frac{1}{2}$ or $\frac{3}{2}$ and it may be shown[8] that

$$a_{1/2}=5a_p-a_s, \tag{3}$$

and

$$a_{3/2}=a_p+a_s, \tag{4}$$

where[9]

$$a_p=\frac{16\mu_N\mu_B}{15I}\int_0^\infty\frac{|P(2p;r)|^2\,dr}{r^3}, \tag{5}$$

and

$$a_s=(16\mu_N\mu_B/9I)\pi\sum_n[\rho_{ns}]. \tag{6}$$

In Eqs. (5) and (6) μ_N and μ_B are the nuclear and Bohr magnetons, respectively. In Eq. (5) $P(2p,r)$ is the one-electron, Hartree-Fock $2p$ orbital,[10] where

$$1=\int_0^\infty|P(2p;r)|^2\,dr. \tag{7}$$

In Eq. (6)

$$\rho_{ns}=|\Psi_{ns\uparrow}(0)|^2-|\Psi_{ns\downarrow}(0)|^2 \tag{8a}$$

where the arrows ↑ and ↓ indicate spin of $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively, and for unpaired s electrons

$$\rho_{ns}=\pm|\Psi_{ns}(0)|^2, \tag{8b}$$

where the + or − sign is chosen to correspond to spin

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of $+\frac{1}{2}$ or $-\frac{1}{2}$. The summation in Eq. (6) is over all pairs and also over all unpaired s electrons as indicated by Eqs. (8a) and (8b), respectively. In Eqs. (8) Ψ_{ns} is the one-electron, Schrödinger ns orbital.

For ions with no unpaired s electrons we see from Eqs. (8) and (6) that there will be no contributions to the hyperfine constant from the s electrons unless we employ "spin-polarized" functions where $\Psi_{ns\uparrow}$ and $\Psi_{ns\downarrow}$ are spatially different.[11] In fact, in many instances one can only obtain nonzero values of the hyperfine fields by employing spin-polarized functions.[12] The inadequacy of the nonpolarized, one-electron representation was recognized some time ago. Fermi and Segrè[13] attempted to remedy this by using configuration interaction techniques to obtain contributions from the 6s shell of Tl due to the presence of the 6p electron. It was subsequently shown[14] that contributions from all core s electrons should be considered. These results would thus seem to lend validity to the concept discussed by Slater,[15] of spin or exchange polarization of core s orbitals by outer orbitals.

Many calculations[9,12,16–23] have been done with spin-polarized functions. All of these have used determinantal wave functions based on a single spin configuration. Hereafter this shall be referred to as the single-determinant approximation. Several inadequacies of the spin-polarized functions, and in particular their use in determining the hyperfine structure constant, led Berggren and Wood[24] to seriously question the validity of the core polarization concept. While it was subsequently shown[25] that their analysis, involving the lithium atom, was not sufficient to invalidate the concept, some deficiencies remain. These deficiencies are:

1. The total energy as calculated with a polarized or nonpolarized function is hardly different. Since we use this criterion of total energy as a test of the "goodness" of a function, then it would seem that we may have merely restructured the wave function to suit a particular calculation without improving the function in general.

2. The spin-polarized functions are no longer exact eigenfunctions of $\mathbf{S}^2$. There has been much discussion as to whether this is significant[8,26–29] in the determination of hyperfine structure. At any rate, the departure from exactness in some specific cases has been shown[12] to be small.

3. In calculations of the hyperfine constant using the single-determinant spin-polarized functions large numerical cancellations occur in the determination both of ρns of Eq. (8a) for an (ns) pair[9] and in the sum of ρns pairs[30] of Eq. (6). We are thus required to carry a large number of significant digits in the evaluation of the orbitals to compensate for these cancellations.

In this paper a two-determinant function based on the spin configurations $\alpha\beta\alpha\beta\cdots\alpha$ and $\beta\alpha\beta\alpha\cdots\alpha$ is proposed. Results of the application using modified Slater orbitals for boron are given. In conclusion, we see that this approximation improves, significantly, the total energy and alleviates, considerably, the cancellation difficulty for ρ_{ns} pairs. In addition, the calculated value of electron charge density at the nucleus, and hence a_s, is changed in the direction required. We can draw no conclusion for changing the cancellation difficulties for sums of ρ_{ns} pairs as we have only two such pairs here while cancellation difficulties only become significant when several such pairs are involved. While we do not resolve the spin eigenvalue problem, it is pointed out that such a resolution demands a great deal more complexity than we are presently able to consider.

TWO-DETERMINANT APPROXIMATION

It has been suggested[25] that a significant improvement over a single-determinant approximation could be obtained by assuming a two-determinant function derivable from the spin configurations $\alpha\beta\alpha\beta\cdots\alpha$ and $\beta\alpha\beta\alpha\cdots\alpha$. The particular selection of these two determinants was made in the light of conclusions arrived at in the discussion of the core polarization effect in the ($1s$, $1's$) $2s$ configuration of the lithium atom. It was shown that of the three spin functions $\alpha\beta\alpha$, $\beta\alpha\alpha$, and $\alpha\alpha\beta$, the last function's contribution both to total energy and to hyperfine energy was negligibly small. Also, since the total number of determinants one may employ is very large[31] it becomes imperative, for practical reasons, to delimit the total number of determinants one uses. Thus we limited our choice to two spin functions $\alpha\beta\alpha\beta\cdots\alpha$ and $\beta\alpha\beta\alpha\cdots\alpha$ and chose these particular

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two functions in analogy with the results for lithium. More significantly we observe that while the single configuration $\alpha\beta\alpha\beta\cdots\alpha$ introduces exchange correlation between the valence orbital and core orbitals of like spin, the addition of the configuration $\beta\alpha\beta\alpha\cdots\alpha$ adds the exchange interaction between the valence orbital and all the other core orbitals. These two determinants represent the optimum (in terms of total number of determinants) way of including exchange polarization between the polarizing orbital and all the polarized orbitals.

THE BORON ATOM

The boron atom in a $(1s, 1's)(2s, 2's)2p$ configuration is a good test case for the two-determinant approximation, since the valence electron cannot mask the core contributions from the s electrons as is the case for lithium.[24] At the same time, the boron atom is sufficiently small so that the calculations are not unduly cumbersome. Thus our wave function is

$$\Phi = NA_P\{U_{1s}\alpha U_{1's}\beta U_{2s}\alpha U_{2's}\beta U_{2p}\alpha + BU_{1s}\beta U_{1's}\alpha U_{2s}\beta U_{2's}\alpha U_{2p}\alpha\}, \quad (9)$$

where N is the normalization constant, A_P the antisymmetrizing operator, and B a structure parameter to be determined variationally. The radial one-electron functions are those of Morse, Young, and Haurwitz[32]:

$$U_{1s} = N_{1s}\exp(-\mu ar), \quad (10)$$

$$U_{1's} = N_{1's}\exp(-\mu a'r), \quad (11)$$

$$U_{2s} = N_{2s}[r\exp(-\mu r) - d\exp(-\mu br)], \quad (12)$$

$$U_{2's} = N_{2's}[r\exp(-\mu r) - d'\exp(-\mu b'r)], \quad (13)$$

and

$$U_{2p} = N_{2p}r\exp(-\mu cr). \quad (14)$$

TABLE I. Wave-function parameters.

Parameter	One determinant $B=0$ Nonpolarized	Polarized	Two determinant $B=0.99525861$ Polarized
a	3.61538	3.55100	2.90163
a'	3.61538	3.55500	4.13280
b	3.30769	3.19500	2.66689
b'	3.30769	3.19300	3.49169
c	0.930769	0.91300	0.90960
μ	1.30000	1.32013	1.33085

TABLE II. Energy and hyperfine constants.

	One determinant Non-polarized	Polarized	Two determinant Polarized	Experiment[a]
ρ_{1s}	0	−0.11094	−0.856309	$\cdots$
ρ_{2s}	0	+0.00619	+0.00109170	$\cdots$
a_s	0	−49.96	−40.3344	0.11
a_p	53.86	53.23	53.93	73.24
$a_{1/2}$	269.30	316.10	309.97	366.09
$a_{3/2}$	53.86	3.265	13.60	73.35
E (a.u.)	−24.5023	−24.5028	−24.5271	−24.66

[a] For hyperfine constants see Ref. 33 and for total energy see Ref. 34.

The constants d and d' are used to orthogonalize the $1s$–$2s$ and $1's$–$2's$ functions, respectively, while the scale factor is chosen so that the solution satisfies the virial theorem. While we almost certainly would have obtained closer agreement with experiment had we used the expanded basis set of Bessis *et al.*,[8] we chose this particular set of orbitals to obtain a relatively facile consistent standard of comparison between the one- and two-determinant, nonpolarized and polarized functions. As the discussion of the results indicates this choice is amply justified.

RESULTS

The wave function parameters of Eqs. (9)–(14) are given in Table I and the hyperfine constants and energy are listed in Table II. The experimental values of the hyperfine constants are from Wessel[33] while the experimental energy is taken from Scherr *et al.*[34] The physical constants are from the compilation of Cohen *et al.*[35] with the exception of the nuclear magneton, $\mu_N = 2.68858$, which is given by Ramsey.[36]

DISCUSSION AND CONCLUSIONS

A glance at Table II shows that we have accomplished our purpose of improving the total energy with the two-determinant representation. In fact, despite the crudity of our orbitals the energy value differs only slightly from the Hartree–Fock value[8] of −24.529.

It will be observed from Table II that the value of a_s is written to six significant digits for the two-determinant approximation while only four significant digits remain in the one-determinant spin-polarized function. In both instances eight digits were main-

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tained in the energy calculation, enabling us to determine the exponential coefficients a, a', b, b', and c to six significant digits. The loss of significant digits in the one-determinant function and the retention of six significant digits in the two-determinant function can most easily be seen by a consideration of the determination of ρ_{1s}. For either function $\rho_{1s} \propto (1-B^2)(a^3-a'^3)$. The source of digital loss in the one-determinant function is apparent from Table I. It is also obvious from Table I that this source of digital loss is not effective in the determination of ρ_{1s} by the two-determinant approximation. In the determination of $(1-B^2)$ in the two-determinant function we lose two significant digits, but since we are able to determine B to eight significant digits, we are able to calculate ρ_{1s} in this case to six significant digits. In the calculations we did not determine B directly but rather a quantity δ such that $B=(1-\delta)/(1+\delta)$. We found that δ could be written as a power series in the difference of the energy as determined by each of the two determinants. This energy difference is merely the difference in the exchange interactions of the primed and unprimed core orbitals with the valence orbital. If the difference was 0, then δ would be 0 and B would be 1 so that ρ_{1s} would be 0. Thus the nonzero value of ρ_{1s} is directly attributable to the difference of the exchange interaction of the core orbitals with the valence orbital, thereby reinforcing the concept of the core polarization effect[15] in hyperfine structure.

By reference to Table II, we also note that a_s is changed in the right direction. Neither value is very close to the experimental value, but simple one- or two-exponent orbitals are known to be very poor in the vicinity of the nucleus and all we are really concerned with here is whether or not, for a given set of one-electron orbitals, we can improve our ability to determine a_s. As the results show, we have attained that improvement. The value of a_p hardly changes. This merely says, essentially, that we have done nothing to improve our representation of the $2p$ orbital, and hence of a_p, but we did not intend here to correct any defects in the determination of a_p. The quantity $a_{1/2}$ (which is more dependent on a_p than a_s) is hardly changed (although slightly worse) in the two-determinant case, while $a_{1/2}$ (which is more dependent on a_s) is closer to the experimental value in the two-determinant representation.

In comparing our spin-polarized results to our nonpolarized results, it would seem from Table II that all we have accomplished is to improve our determination of $a_{1/2}$ at the expense of $a_{3/2}$. It must be remembered, however, that we must use polarized functions in order to obtain a nonzero value of a_s as deduced from the experimental values of $a_{1/2}$ and $a_{3/2}$. Also, all we have set out to show is that for a given basis set we can more easily determine a_s while at the same time improve the total energy with the additional determinant in a spin-polarized representation. Furthermore, it has already been shown[8] that improved values of the hyperfine constants are obtainable using improved basis sets and as the preceding discussion indicates we should not expect to improve significantly these calculated values of the hyperfine constants in a two-determinant representation, but rather we should expect to be able to determine the constants more easily. Further improvements would require, for example, the introduction of basic sets, including interelectronic separation terms.

We can thus conclude that a two-determinant representation can be expected to improve the total energy and alleviate the cancellation difficulties in the determination of individual ρ_{ns} pairs. In addition, we can conclude that we are able to determine a_s more easily in a two-determinant representation. We still have the problem that neither the one- nor two-determinant representation are eigenfunctions of $\mathbf{S}^2$. A calculation based upon a four-determinant function constructed from the spin configuration $\alpha\beta\alpha\beta\alpha-\alpha\beta\beta\alpha\alpha+\beta\alpha\beta\alpha\alpha-\beta\alpha\alpha\beta\alpha$ has been performed. This is an eigenfunction of $\mathbf{S}^2$. The calculated value of a_s was identically zero. It would thus seem that we would have to use a spin configuration involving terms like $\alpha\alpha\alpha\beta\beta$, $\alpha\beta\alpha\alpha\beta$, etc. It can be shown[37] that one can always set up a proper eigenfunction configuration involving all possible antiparallel spin pairs and another proper spin eigenfunction configuration involving a sum of one set of parallel spins for every pair in addition to terms involving all antiparallel spin pairs. The number of determinants thereby generated is very large and since the two-determinant approximation does very well there hardly seems any need at present to get more involved.

It remains to be seen whether we can correct for the cancellation in summation over ρ_{ns} pairs and the affect of the approximation using an improved orbital representation. These determinations are presently underway.

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[37] E. A. Burke (unpublished). The proof is available on request.